

SYNTHESIS AND THERMAL STABILITY OF CONJUGATED POLYMER OF 1, 2-DICHLORO BENZENE AND NAPHTHALENE

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ABSTRACT

The co-polymer (Poly-CIBN) of 1, 2 Di-ChloroBenzene and Naphthalene has been synthesised. The copolymer (Poly-CIBN) has been characterised by X Ray Diffraction (XRD) and UV spectroscopic method. Thermo Gravimetric analysis (DTA, DTG and TG) has been used for analysis of thermal stability of the copolymer.

KEYWORDS: Thermal Stability, XRD, Thermo Gravimetric Analysis, (DTA, DTG and TG), UV Spectroscopy, 1,2 Di-ChloroBenzene, Naphthalene, Conjugated Polymer

INTRODUCTION

Conjugated¹ polymers are composed of a long repeating chain of similar smaller molecules called monomers. These are polymers which consist of delocalized Π - electron system along the polymer backbone. The delocalized Π – electron system contains semi-conducting properties to the polymer and gives it the ability to support positive and negative charge carrier with high mobility along the polymer chain. The semi conducting properties of the materials arise from the overlap of p_z – orbital, which originate from the double or triple bonds. If the overlap is over several sites, the formation of well delocalized Π valance and Π^* conduction bands occurs, with an energy gap in between and this recipe for this semi conducting behaviour. The^A principal interest in the use of polymers lies in the scope for low-cost manufacturing, using solution-processing of film forming polymers.

One of the main advantages of these materials is the way they are processed to form thin films. Whereas conventional inorganic semiconductors are usually deposited from the gas phase by sublimation or evaporation, conjugated polymers can be processed from solution (e.g. by spin-coating or printing techniques). That makes this class of materials combine the optoelectronic properties of semiconductors with the mechanical properties and processing advantages of plastics.

Fundamental² differences among organic and inorganic devices result from differences between inorganic and molecular semiconductor materials. No charges are present in OLED devices without charge injection. Emission is due to radiative transitions from the neutral excited states to the ground states. We pointed out the important role that the OLEDs play in display design (even the flexible ones) Some of the frequently used conjugated polymers, in LED (Light Emitting Diode) are, poly (p – phenylene) (ppp) and poly (p – phenylenevinylene) (ppv).

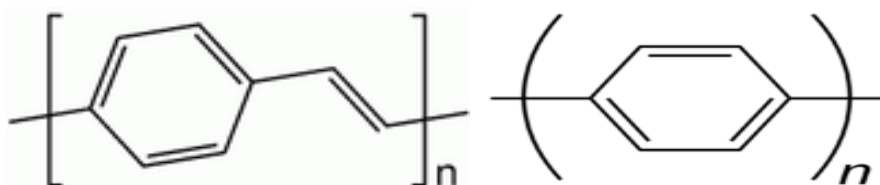


Figure 1: Poly (p – Phenylenevinylene) (ppv).Poly (p – Phenylene) (ppp)

The poly (p – phenylene) is insoluble in solvents and has unprocessibility. To overcome this problem there is need to synthesize other conjugated co-polymers such as substituted benzene – naphthalene polymer, PPEs, poly (arylene ethylene) PAE etc. among a variety of materials of platforms; poly (arylene ethylene) (PAE) derivatives have attracted the attention of a growing number.

In the present work we synthesized Co-polymer of 1,2 Di-ChloroBenzene with Naphthalene .We also found out that the resulting polymer is fluorescent and show electroluminescence property. We have characterized the polymer using X Ray Diffraction(XRD) and UV spectroscopic method. Thermo Gravimetric analysis (DTA,DTG and TG) has been used for analysis of thermal stability of the copolymer.

THEORITICAL DETAILS

Naphthalene

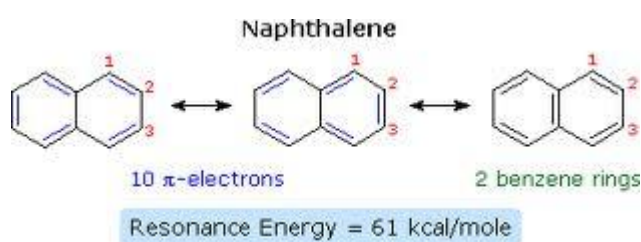


Figure 2

[Resonance Structure of Naphthalene]

Substitution occurs at the “alpha” position in naphthalene and other similar structures.

Rationalization

Regioselectivity in electrophilic aromatic substitution depends on the stability of the cationic intermediate. If we compare the two competing pathways, we notice that we can write several resonance structures for each of the two cationic intermediates. However, the action resulting from alpha addition (top) has one contributing structure that retains the unbroken benzene-like structure whereas the action from beta addition (bottom) does not have any benzenoid contributing structures.

Because the benzenoid bonding pattern is associated with aromatic stabilization, we conclude that the preferred pathway of addition will be the one that retains the greatest number of intact benzene-like rings among its resonance structures.

A Naphthalene molecule is composed of two fused benzene rings (rings are fused if they share two or more atoms). Accordingly naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH).

There are two sets of equivalent hydrogens-

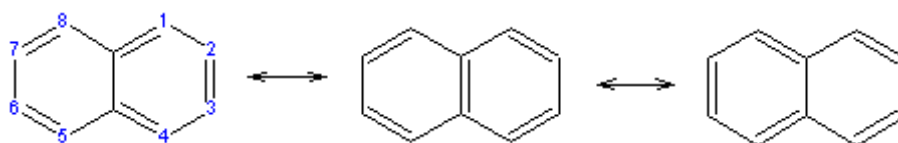


Figure 3

- Alpha Hydrogen - The alpha positions are 1, 4, 5 and 8
- Beta Hydrogen - Beta positions are 2, 3, 6 and 7 phthalic acid.

Physical Properties

- Chemical formula: $C_{10}H_8$
- Molecular weight: 130 g/mol
- Melting point: 80.2 °C
- Boiling point: 218 °C
- Resonance energy: 2.651 eV
- Density: 1.14 g/cm³

1, 2 Di- Chloro Benzene

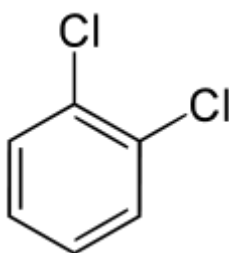


Figure 4

1,2-Dichlorobenzene, or **orthodichlorobenzene** (ODCB), is an organic compound with the formula $C_6H_4Cl_2$. This colourless liquid is poorly soluble in water but miscible with most organic solvents. It is a derivative of benzene, consisting of two adjacent chlorine centers

Table 1

Physical Properties	
Molecular formula	$C_6H_4Cl_2$
Molar mass	147.01 g/mol
Density	1.30 g/cm ³
Melting point	-17.03 °C, 256 K, 1 °F
Boiling point	180.5 °C, 454 K

Solubility :soluble in most organic solvents

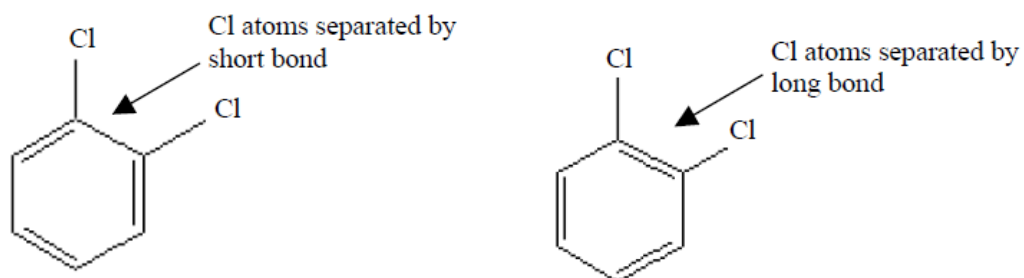


Figure 5

According to the structure proposed by Kekulé, there should be two isomers of 1,2-dichlorobenzene. In one structure, the chlorine atoms are separated by a single bond, and in the other, they are separated by a double bond. However, these isomers have never been isolated or detected.

THERMAL ANALYSIS

- A group of analytical techniques
- Each technique defines a material property
- physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program"
- Heat flow into a substance induces many physical and chemical changes which can help to identify and characterize a sample

Differential Thermal Analysis (DTA)--Heat of Transitions

The material under study and an inert reference are made to undergo identical thermal cycles. Any temperature difference between sample and reference is recorded. In this technique the heat flow to the sample and reference remain the same rather than the temperature. The differential temperature is then plotted against time, or against temperature (DTA curve or thermogram). In an endothermic event takes place within the sample, the temperature of the sample will lag behind that of the reference and a minimum will be observed on the curve. On the contrary, if an exothermal event takes place, then the temperature of the sample will exceed that of the reference and a maximum will be observed on the curve. The area under the endotherm or oxotherm is related to the enthalpy of the thermal event, ΔH .

Derivative Thermogravimetric Analysis (DTG)

Derivative thermogram plots changes in mass with temperature dm/dt and resolves changes more clearlyTG Thermal Gravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) or Thermogravimetry

Principle --Changes in the mass of a sample are studied while the sample is subjected to a controlled temperature programme. The temperature programme is most often a linear increase in temperature, but, isothermal studiesalso be carried out, when the changes in sample mass with time are followed. TGA is inherently quantitative, and therefore an extremely powerful thermal technique, but gives no direct chemical information. The ability to analyze the volatile products during a weight loss is of great value.

X-RAY DIFFRACTION (XRD)

Morphology⁸ of conjugated polymers has been primarily analyzed through atomic force microscopy (AFM) and x-ray diffraction (XRD).] XRD provides information on the spacing and orientations of crystal planes.

EXPERIMENTAL DATA

The synthesis of the co-polymer of naphthalene and 1, 2 Di-chlorobenzene (poly-CIBN) has been carried out by the conventional Kovacic method using a $FeCl_3$ as catalyst. The heterogeneous reaction mixture consisting of the, catalyst,1,2Dichlorobenzene and naphthalene is stirred for 4–6 hrs at 35-40°C.After the completion of the reaction, the reaction mixture is washed with distilled water in order to remove the impurities .The orange brown polymer obtained is dried under vacuum..The characterization of the resultant polymer has been carried out by spectroscopic techniques.

Drying: The polymer was then dried at a temperature of about 40°C in a dessicator. After drying it became orange brown in color.

Solubility: The polymer was insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran (THF), Chlorobenzene, NMP, Xylene etc.

Characterization of Co-Polymer of 1, 2Di-Chloro Benzene and Naphthalene

UV-VIS Absorption Spectra of the Co-Polymer of 1,2 Di Chloro Benzene and Naphthalene

UV-VIS Spectra of the Co-polymer of 1,2 Di-Chloro benzene and naphthalene was recorded on a shimadzu UV-2401 Spectrophotometer. The absorption spectrum of the co-polymer in Chloroform exhibit absorption bands in UV regions, which are identical to the absorption spectrum of poly p-phenylene (PPP). The absorption band appears to be vibronic spectra of naphthalene molecules shift owing to its attachments on poly p-phenylene chain.

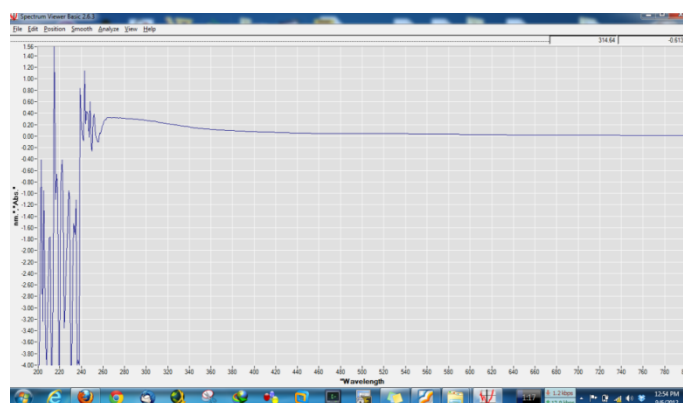


Figure 6

UV-VIS absorption Spectra of the Co-polymer of 1,2DiChlorobenzene and Naphthalene

Thermogravimetric Analysis

Thermogravimetric analysis of the co-polymer shows that the thermal stability of the co-polymer in comparison to the parent polymer poly-p-phenylene is significantly lower.

Poly-p-phenylene was thermally stable up to 450 Cel under ambient conditions, whereas the co- polymer was found to be thermally stable only up to 337 Cel . A weight loss at 199 Cel might be attributed to the loss of some adsorbed water molecules onto the polymer. The sharp weight loss from 350 to 836 Cel may be attributed to the decomposition of the polymeric back bone (Table 1).

Table 2: Thermal Analysis of Data of Co-Polymer of 1,2 DiChlorobenzene and Naphthalene

STEP	T _{range(cel)} TG	T _{peak(cel)} DTG	Loss of Mass %
1	100-300	199	15.38
2	300-400	337	5.69
3	800-900	836	9.83

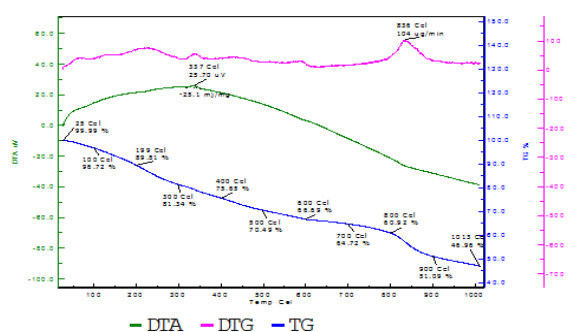


Figure 7

Sample Name: Distilled Water
 Data Name: A-Sudha-1
 Measurement Date: 4/29/2013
 Sample Weight: 7.047 mg
 Reference Weight: 10.500 mg
 Reference Name: Alumina Powder
 Instrument: EXSTAR TG/DTA 6300
 Operator: A. K.Saini
 s1: Nitrogen (200ml/min)
 Gas2:
 Pan: Alumina
 Inst No. 1

In DTA curve exothermic peak at 337cel is due to the decomposition of co polymer and it is well above the heating temperature employed in present work.

The area under the exotherm is related to the enthalpy of thermal event $\Delta H = -25.1 \text{ mj/mg}$

X-Ray Diffraction Analysis (Xrd)

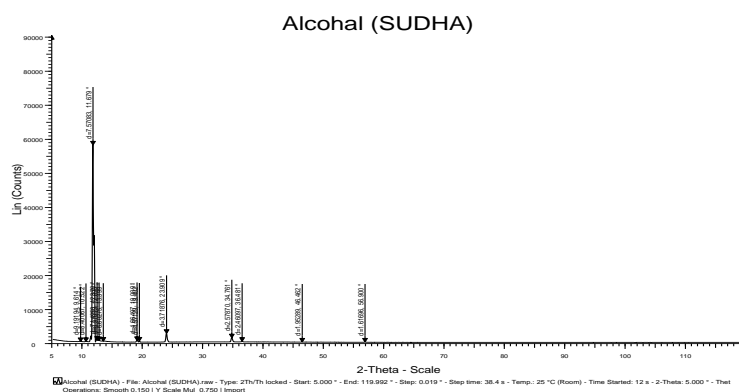


Figure 8

Caption Legend	Angle	d value	Intensity	Intensity %	h	k	l
	2-Theta °	Angstrom	Count	%			
	d=9.19194, 9.614 °	9.614	9.19194 434	0.7			
	d=8.40067, 10.522 °	10.522	8.40067 447	0.8			
	d=7.57083, 11.679	11.679	7.57083 58427	100.0			
	d=7.14950, 12.370 °	12.370	7.14950 826	1.4			
	d=6.97013, 12.690 °	12.690	6.97013 709	1.2			
	d=6.60275, 13.399 °	13.399	6.60275 534	0.9			
	d=4.66497, 19.009 °	19.009	4.66497 732	1.3			
	d=4.57129, 19.402 °	19.402	4.57129 592	1.0			

$d=3.71876, 23.909^\circ$ 23.909 3.71876 2845 4.9

$d=2.57870, 34.761^\circ$ 34.761 2.57870 1531 2.6

$d=2.46097, 36.481^\circ$ 36.481 2.46097 495 0.8

$d=1.95289, 46.462^\circ$ 46.462 1.95289 291 0.5

$d=1.61696, 56.900^\circ$ 56.900 1.61696 304 0.5

d = Interplaner distance between two consecutive planes of polymer.

Electron density at angle 2θ

Intensity of diffraction is maximum at

$d=7.57083$

$2\theta=11.679^\circ$

This clearly shows the maximum electron density at this point and electron density of conjugated polymer decreases thereafter.

RESULTS & DISCUSSIONS

Co-polymer of 1,2Dichlorobenzene and naphthalene has been prepared as a soluble poly-phenylenederivative. The polymer obtained is orange brown and soluble in organic solvents like chloroform, toluene and *N*-methylpyrrolidone. The reaction can be represented as

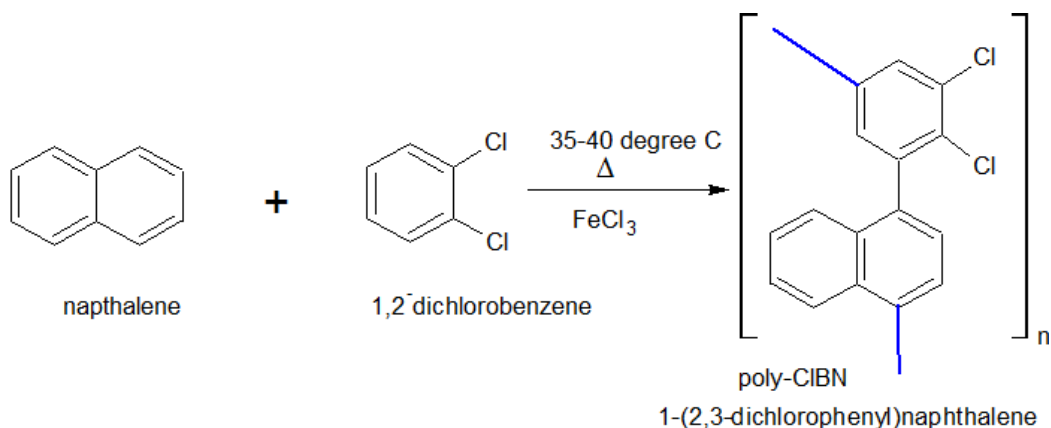


Figure 9

The (Poly-CIBN) conjugated polymer is synthesized and characterized by using various techniques such as UV, DTA,DTG , TG and XRD which are discussed as above.

CONCLUSIONS

We have synthesized a new co-polymer Incorporating 1,2-Dichloro benzene and naphthalene, which has practical utility in the fabrication of OLEDs. The new polymer is soluble in common organic solvents and can be thermally evaporated to make thin films.. Therefore, the synthesized materials have good prospects for the industrial applications as electroluminescent materials in coming days.

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